Federal Advisory Committee on Detection and Quantitation Approaches and Uses in EPA's Clean Water Act Programs

Common Base of Information

June 21, 2005

Presentation Overview

- EPA and Clean Water Act (CWA) mandates
- Statutory authority for analytical methods in EPA's CWA programs
- History of detection and quantitation
  - Chronological
  - Emphasis on history in EPA's CWA programs
- Where we are today

EPA and Clean Water Act Mandates

- EPA's mandate is to "protect human health and the environment"
- CWA's mandate is to "restore and maintain the chemical, physical, and biological integrity of the Nation's waters"
  - Detection and quantitation limits must support these mandates
    - Examples
      - Measurements need to be made at ambient water quality criteria levels to assure protection of aquatic life
      - Measurements need to be made to support waste load allocations for total maximum daily loads (TMDLs)

Congressional Authority for Analytical Methods

- Clean Water Act (CWA) Sections 301(a), 304(h), and 501(a) provide the statutory authority for test procedures (analytical methods)
  - Section 301(a) prohibits discharge of a pollutant without a permit
  - Section 304(h) requires EPA to promulgate guidelines establishing test procedures for the analysis of pollutants
  - Section 501(a) authorizes the EPA Administrator to prescribe regulations necessary to carry out CWA functions
- CWA methods are promulgated at Title 40, parts 136 and 405 – 599, of the *Code of Federal Regulations* (CFR), written as, e.g., 40 CFR part 136

Characteristics of an Analytical Method

- In environmental analytical chemistry, a *method* is a series of steps (a *procedure*) that leads to a *result* (concentration or amount) for an *analyte* in a *sample*
- Method performance characteristics include
  - Precision
  - Recovery
  - Specificity
  - Detection and quantitation limit (sometimes termed “sensitivity”)

Detection/quantitation Limit History

- Seminal work on detection and quantitation is by Lloyd Currie, recently retired from NIST
  - Published in *Analytical Chemistry* in 1968 (**40**, p586)
  - Introduced terms of
    - "critical level" (L_C), "critical value" (CRV); the "detection decision"; sometimes "detection limit"
    - "minimum detectable value" (MDV), "detection limit" (L_D)
    - "determination limit", "minimum quantifiable value" (MQV); limit of quantitation" (LOQ); commonly "quantitation limit" (L_Q)
  - Currie's work forms the basis the ISO/IUPAC nomenclature and standards, and nearly all other approaches

Detection/quantitation History – ML

- On December 3, 1979, EPA proposed the 600-Series organic methods (44 FR 69463)
  - GC/MS Methods 624 and 625 contained a “limit of detection” for each compound
    - In Method 624, the LOD was defined as defined as the “minimum level at which entire system must recognizable mass spectra and acceptable calibration points”
    - In Method 625, the LOD was defined as the “minimum level at which the analytical system must give mass spectral confirmation.”
  - The LOD in Methods 624 and 625
    - Were estimates of the lowest level that could be measured and the basis for the minimum level of quantitation (ML)

Detection/quantitation Limit - MDL

- Method detection limit (MDL) was first published in a paper by John Glaser and others at EPA's laboratory in Cincinnati in 1981 in *Environmental Science and Technology* (**15**, p1426)
  - MDL based on Currie's work
  - Employs low-level spikes rather than backgrounds
  - Uses Student's t-test to allow for varying number of replicates
  - Has remained largely unchanged since publication

MDL and ML Promulgation

- On October 26, 1984 (49 FR 43234), EPA promulgated:
  - The 600- and 1600- Series organic methods at 40 CFR 136, appendix A
    - The 600-Series methods contained MDLs as detection limits
    - Methods 1624 and 1625 contained MLs as detection limits
  - The MDL procedure at 40 CFR 136, appendix B
  - Method 200.7 for metals at 40 CFR 136, appendix C
    - Method 200.7 contained MDLs as detection limits

Detection/quantitation - ACS

- In 1980 and 1983, the American Chemical Society's (ACS's) Committee on Environmental Improvement adopted an approach similar to Currie's
  - "Limit of detection" (LOD) nearly identical to Currie's "critical value" (L_C) and EPA's MDL
  - "Limit of quantitation" nearly the same as Currie's "limit of quantitation" (L_Q)

VEPCO Suit and Settlement

- In early 1985, members of the power industry brought suit against EPA
  - The suit claimed, among other things, that the MDL procedure in appendix B should be applicable to the organic methods in appendix A only
- On July 12, 1985, EPA signed a settlement agreeing to industry's condition
- The settlement did not preclude future use of the MDL by EPA or the right of the litigants to bring suit over future use

Use of ML in OCPSF Rule

- On November 5, 1987 (52 FR 42522), EPA published a final rule for the Organic Chemicals, Plastics, and Synthetic Fibers (OCPSF) industrial category
  - The rule was the first use of the ML as an effluent limit and data censoring point
    - Data below the MLs listed in Methods 1624 and 1625 were not considered in calculating effluent limits
    - No limit was set below 10 µg/L (parts-per-billion)
    - Significant because MDLs were not used for effluent limits or regulatory compliance; instead, MLs were used
  - Nearly all subsequent effluent guidelines were censored to the ML

WQBEL Guidance

- In 1994, EPA published draft “National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-based Effluent Limitations Set Below Analytical Detection/Quantitation Levels” (WQBEL Guidance)
  - Guidance suggested use of the ML as a compliance evaluation threshold when the ambient water quality criterion was below the detection limit of the most sensitive analytical method
    - Concerns
      - Industry - ML too low
      - States - ML not as protective as the MDL.
    - EPA did not complete the WQBEL Guidance, but it precipitated further discussions of detection and quantitation limits

Refinement of ML

- In support of the draft WQBEL Guidance, EPA refined the ML to be consistent with the ISO/IUPAC LOQ (at the time) and the ACS LOD
  - ML = 10 times the standard deviation of 7 replicates
    - ML = 3.18 times the MDL

ASTM IDE and IQE

- In the mid- to late- 1990s, Robert Gibbons, David Coleman, Nancy Grams, and others worked through IIAG and within ASTM Committee D19 to develop the “interlaboratory detection estimate” (IDE) and “interlaboratory quantitation estimate” (IQE)
  - IDE and IQE used a model of standard deviation or relative standard deviation (RSD) as a function of concentration as the basis for establishing detection and quantitation estimates

EPA Method 1631 for Mercury

- On June 8, 1999 (64 FR 30417), EPA promulgated Revision B to EPA Method 1631 for determination of mercury by purge-and-trap and atomic fluorescence
  - The Alliance of Automobile Manufacturers, Inc. and others brought suit over, among other things, the detection and quantitation limits in EPA Method 1631 and how they were developed

Settlement Agreement

- In Clause 6 of a Settlement Agreement signed October 19, 2000, EPA agreed to:
  - Re-assess procedures for determining detection and quantitation limits
  - Peer review the re-assessment
  - Provide opportunity for comment on the re-assessment
  - Publish a notice and invite comment on the re-assessment by February 28, 2003
  - Publish a notice of final action on the re-assessment by September 30, 2004

Evaluation of Concepts

- Evaluation criteria for detection and quantitation
  - The concept must be scientifically valid
    - It can and has been tested
    - It has been subjected to peer review and publication
    - It is supported by a well-defined procedure
    - It has been accepted by the scientific community
    - The error rate is known or can be estimated
  - The concept must include routine variability
  - The concept must be applicable in a single laboratory
  - The detection limit concept should identify the concentration at which there is 99% confidence that the analyte is present

Evaluation of Concepts (cont'd)

- Evaluation criteria for detection and quantitation (cont'd)
  - The quantitation limit should identify the concentration at which the reliability of the measurement is consistent with the capabilities of a method practiced by an experienced staff in a well-operated laboratory
  - Detection and quantitation limits must be applicable to the variety of decisions made under CWA, and should support State and local obligations to implement measurement requirements at least as stringent as those set by the Federal Government

Datasets Used in the Evaluation

- EPA evaluated each concept using datasets developed by EPA or submitted to EPA
  - Four studies ranging from simple → complex
  - Evaluated more than 11 analytical methods over wide concentration range

Federal Register Proposal

- On March 12, 2003 (48 FR 11770), EPA published a proposal in the *Federal Register*. The proposal:
  - Met requirements in Clause 6.a. of the Settlement Agreement
  - Announced the availability of the re-assessment
  - Proposed changes to the MDL procedure based on the re-assessment and comments received
  - Proposed codification of the ML procedure at part 136
  - Invited comments on the re-assessment and proposal

Final Re-assessment

- On November 8, 2004 (69 FR 64704), EPA published a "Revised Assessment of Detection and Quantitation Approaches"
  - The revised assessment met requirements in Clause 6.f of the Settlement Agreement
  - The revised assessment was supported by a "revised assessment document" (RAD)

Withdrawal of Proposed Changes to CFR

- Also on November 8, 2004 (69 FR 64707), EPA withdrew:
  - Proposed changes to the MDL procedure
  - Codification of the ML procedure
- EPA announced plans to work with stakeholders to address concerns about calculation and use of detection and quantitation limits in CWA programs
- This action did not change the way EPA calculates MDLs and MLs

Federal Advisory Committee Formation

- On January 26, 2005, EPA held a public meeting to report findings in the "Situation Assessment Report on Detection and Quantitation Approaches and Uses in [EPA's] Clean Water Act Programs" and formation of today's Federal Advisory Committee

- On May 24, 2005 (70 FR 29743), EPA announced today's first meeting of the "Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act (CWA) Programs"

Where we are today

- Lots of background information
  - EPA's detection/quantitation web site (www.epa.gov/waterscience/methods/det)
  - Water Docket (OW-2004-0041)
- Diverse, balanced group representing: States, POTWs, Industry, Laboratories, and Environmental Community
- EPA has a strong commitment to resolve long-standing concerns about detection and quantitation approaches and uses in CWA programs

Additional Information

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